

Supercooled Water and the Kinetic Glass Transition II: Collective Dynamics

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Abstract

In this article we study in detail the Q -vector dependence of the collective dynamics in simulated deeply supercooled SPC/E water. The evolution of the system has been followed for 250 ns at low T , allowing a clear identification of a two step relaxation process. We present evidence in favor of the use of the mode coupling theory for supercooled liquid as framework for the description of the slow α -relaxation dynamics in SPC/E water, notwithstanding the fact that the cage formation in this system is controlled by the formation of an open network of hydrogen bonds as opposed to packing constraints, as in the case of simple liquids.

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I. INTRODUCTION

The slow dynamics (α -relaxation) in supercooled molecular liquids and the glass-transition are two related topics which have received particular attention from the scientific community in the last years [1,2]. Significant progress have been made by a sinergetic approach based on theoretical, experimental and more recently on numerical work. Nowadays, numerical simulations with realistic potentials describing the evolution of molecular system composed by thousand atoms, for time interval longer than 100 *ns*, are becoming feasible, allowing a closer check of the theoretical predictions and bridging the gap between experiments and theory. Such long simulations, although are suffering on the deficiency of the potential used compared to the real systems which they aim to simulate, offer a ideal reference for comparing with the novel theoretical predictions concerning the slow dynamics above the glass transition.

In the case where the studied system is water, the interest in interpreting the molecular dynamics in term of glass-transition concepts goes beyond the comparison between the simulated system and the theoretical predictions. Indeed, if the experimentally observed non-Arrhenius increase of the transport coefficients on supercooling [3,4] can be explained within the same framework of simple supercooled liquids [5,6], the presence of hidden thermodynamics anomalies at ambient pressure [7,8] does not have to be invoked [9,10]. In the first paper of this series [11] we have tested Mode Coupling Theory (MCT) [12] predictions for the correlation functions of single particle dynamics in water with corresponding quantities calculated from Molecular Dynamics (MD) simulations, carried out for sufficiently long time (20 to 50 *ns*) as to allow the slow dynamics to be observed. We tried to assess to what extent the MCT, which has been shown to describe simple liquids [13,14], is applicable also to the description of the single particle dynamics of (simulated) supercooled water, an hydrogen bonded liquid with strong non-isotropic interactions among molecules. As a result we found that the center of mass tagged particle dynamics can be qualitatively interpreted in terms of MCT. This result stimulated us to make the comparison more stringent and to

extend it to the collective center of mass dynamics. With one further year of computer time on three workstations working full-time, the limit of 250 *ns* of continuous simulation time has been reached, allowing the calculation of the collective properties, for which the noise level can not be reduced averaging over different molecules in the simulated system.

Theoretical work based on the MCT has mainly focused on simple atomic liquids and on molecular liquids with spherical-symmetric interactions. Only recently the theory has been extended to treat the case of molecular systems with non-isotropic interaction potentials opening the way for a full and detailed quantitative comparison between theory and simulation/experiments for molecular systems [15]. Unfortunately, preliminary results at the ideal MCT level are only available for dipolar hard spheres [16,17], i.e. molecules with a simpler geometry than the water molecule geometry. Such results [16] strongly supports the validity of general predictions based on the MCT for simple liquids.

In this article we study in detail the Q -vector dependence of the collective dynamics in SPC/E water and present evidence in favor of a MCT description of the slow α -relaxation dynamics. The comparison is performed on a two level scale: (i) At qualitative level, we compare the MCT prediction for simple liquids (exemplified by the hard-sphere liquid within the Percus-Yevick approximation) with the center of mass dynamics in the case of supercooled SPC/E water. Although the comparison is by default qualitative, we think that the analogy in the Q dependence of all relevant parameters is particularly significant. (ii) At quantitative level, we compare the SPC/E slow dynamics with the dynamics predicted by MCT in the late β -region; moreover we evaluate the von Schweidler exponents b and γ governing the relaxation process (Sec.II) and we verify that they are related as MCT predicts.

In both cases the agreement is striking and strongly supports the validity of MCT as the correct framework for interpreting the slow collective dynamics in simulated supercooled water.

II. MCT

Several review papers present in detail the theory of mode coupling for supercooled liquids, in particular in its *ideal* formulation. A review on the predictions of the theory can be found in Ref. [11]. In this section we briefly report the main results which are relevant for the reading of the article.

MCT aims at describing the slow dynamics in supercooled glass forming simple liquids or in molecular liquids with spherical-symmetric interactions between the molecules. It provides a description of the time evolution of density and current correlation functions (correlators in the following) in the time region where structural relaxation becomes the process which entirely controls the dynamics, *i.e.* for times longer than the microscopic characteristic time. MCT describes the slowing down of the structural relaxation, which is typical of supercooled liquids, including memory effects in a memory function which depends only on statical quantities (number density and structure factor $S(Q)$).

In the *ideal* formulation the loss of correlation is ascribed completely to interaction between fluctuations of density pairs; all other channels for the decay of correlation, as for example the momentum modes, are completely neglected. The ideal MCT predicts a sharp liquid to glass transition, located at a finite critical temperature T_c , associated with a power-law divergence of the correlation time. T_c is a purely kinetic transition temperature which describes the freezing of the molecules inside the cages and it does not deal with any thermodynamical anomalous behavior. The *ideal*-MCT can be considered as a first order approximation in a more complex scheme [18]; the kinetic transition is an artifact of the approximations involved and it disappears in the *extended* version of MCT, where couplings with particle momenta are taken into account. The power-law increase of the characteristic times predicted by the ideal MCT for $T > T_c$ crosses to a different (unknown) relation, to describe the complex activated dynamical processes below T_c . The concept of T_c retains the meaning of cross-over temperature between two different dynamical behaviors and the prediction of the ideal MCT can be used to interpret the slow dynamics above T_c , when

hopping effects are negligible.

The ideal MCT predicts the existence of a two step relaxation scenario for the slow dynamics in supercooled simple liquids at temperatures close to T_c . The decay of the correlators, *i.e.* the loss of memory of the initial configuration, occurs in a two-step process [2,19]: first the normalized correlator $\phi(t)$ approaches a plateau value ϕ_{EA} which is temperature-independent (non-ergodicity or Edwards-Anderson parameter); then $\phi(t)$ decays from ϕ_{EA} to zero (α -relaxation region). The short times region is strongly affected by the microscopic dynamics, which instead completely disappears in the long time region (α -relaxation). In the region close to the plateau (β -relaxation region) $\phi(t)$ can be asymptotically expanded near the value ϕ_{EA} :

$$\phi(t) = \phi_{EA} + h\sqrt{\sigma}g(t/t_\sigma) \quad (1)$$

where t_σ is the time scale which characterize the β -region and σ is the separation from the critical point (at fixed number density $\sigma = (T - T_c)/T_c$). The function $g(t/t_\sigma)$ (also called β -correlator) is solution of the asymptotic equation

$$-1 + \lambda \tilde{z} LT[g^2(\tilde{t})](\tilde{z}) + [\tilde{z}g(\tilde{z})]^2 = 0 \quad (2)$$

where $\tilde{t} = t/t_\sigma$ is the scaled time, LT means the Laplace transform and $\tilde{z} = z t_\sigma$ is the Laplace conjugate of \tilde{t} ; λ is the exponent parameter [18].

It's easy to show that Eq. 2 has a scale invariant solution; in the early β -region, *i.e.* for $t \ll t_\sigma$, $g(\tilde{t})$ has, at the leading order, the fractal behavior:

$$g(\tilde{t}) = \tilde{t}^{-a} + O(\tilde{t}^a) \quad (3)$$

In the late β -region ($t \gg t_\sigma$) the predicted scaling law is

$$g(\tilde{t}) = -\tilde{t}^b + O(\tilde{t}^{-b}) \quad (4)$$

The two scaling exponent a and b are not independent; they are both determined by the exponent parameter λ through the relation:

$$\lambda = \frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)} \quad (5)$$

where Γ is the Euler's gamma function. The range of validity of these expansions for $g(\tilde{t})$ is limited at small t by the microscopic dynamics time and at large t by the α -relaxation time.

In the α -relaxation region another time scale appears, τ ; in terms of the rescaled time $\hat{t} = t/\tau$ the behavior of the correlator near the plateau is described in the leading order by a power law dominated by the exponent b . Including the next to leading order corrections the departure from ϕ_{EA} in the early α -relaxation region is given by

$$\phi(t) = \phi_{EA} - h_{(1)}\hat{t}^b + h_{(2)}\hat{t}^{2b} + O(\hat{t}^{3b}) \quad (6)$$

The amplitudes $h_{(1)}$ and $h_{(2)}$ strongly depend on the physical features of the studied liquid and they have been explicitly calculated for a few models [20,21]. The α -relaxation time scale is a temperature dependent parameter which scales as the inverse of diffusivity:

$$\tau(T) \sim |T - T_c|^{-\gamma} \quad (7)$$

with

$$\gamma = 1/2a + 1/2b \quad (8)$$

The three scaling exponents a , b and γ are not universal since they depend on the static structure factor. In the α -relaxation region the correlators obey the so-called time-temperature superposition principle, i.e. it is possible to scale the same correlator evaluated at different T on a single master curve, i.e.

$$\phi(t) = \phi(t/\tau(T)) \quad (9)$$

For times much longer than τ the mode-coupling dynamical equations can not be solved either analytically nor asymptotically. From numerical solutions developed for simple potentials it has been shown that a Kohlrausch-Williams-Watts (KKW) stretched exponential form, i.e.

$$\phi(t) = A_K \exp[-(\frac{t}{\tau_K})^{\beta_K}] \quad (10)$$

can be used to empirically fit the last part of the $\phi(t)$ decay.

If we specialize the previous equations to the case in which ϕ is the intermediate scattering function $F(Q, t)$, the self correlation function $F_{self}(Q, t)$ or the transverse current correlation $J_t(Q, t)$, the non-ergodicity factor ϕ_{EA} , the critical amplitudes h , $h_{(1)}$, $h_{(2)}$, and the fitting parameters τ_K , β_K becomes Q -dependent quantities. Therefore the comparison between theory and experiments can be extended from the time dependence of ϕ and the temperature dependence of the correlation times to the Q -dependence of the above mentioned parameter.

The MCT set of coupled integro-differential equations can be numerically solved once the static structure factor $S(Q)$ is known. The problem has been solved for many different potentials: hard spheres [20,22], soft spheres [23], Lennard-Jones [24], binary mixtures of soft spheres [25] and of Lennard-Jones [26]. For all these potentials the Q -dependence of the quantities appearing in the previous equations as well as the fitting parameters (τ_K and β_K) in Eq. 10 shows pronounced oscillations in phase with $S(Q)$.

Moreover it has been shown theoretically [2,19,18] that the large Q limit of the fitting parameters β_K coincides with the scaling exponent b .

III. SIMULATION DATA

The MD data analyzed in this article are a series of 250 ns long trajectories for a system of $N=216$ water molecules interacting with the SPC/E potential with periodic boundary conditions. SPC/E, one of the most common water-water potential, is a pair-wise additive potential designed to mimic the interaction between *rigid* water molecules via electrostatic and Lennard-Jones interactions. The simulation technique has been discussed in detail in Ref. [11] and it is not repeated here. The only difference between the data analyzed in this article and the data analyzed in Ref. [11] is the length of the simulation which now cover a time interval more than 5 times longer. We study seven different temperatures, ranging from $T = 207K$ up to $285K$.

IV. ANALYSIS

The basic quantity in the study of the center of mass collective dynamics in a liquid is the coherent intermediate scattering function, defined as

$$F(\vec{Q}, t) = \frac{1}{S(Q)} \sum_{j,k=1}^N e^{-i\vec{Q}[\vec{r}_k(t) - \vec{r}_j(0)]} \quad (11)$$

where N is the number of molecules in the system, \vec{Q} is the wavevector and \vec{r}_i is the position of the center of mass of molecule i . $F(\vec{Q}, t)$ is the autocorrelation function of the space-Fourier transform of the density, thus giving information on the decay of density fluctuations at wavevector Q .

The T and Q dependence of $F(Q, t)$ are shown in Fig.1 and 2. We show the T dependence at two different Q vectors, namely (i) the $Q = 18nm^{-1}$ vector, corresponding to the position of the first pre-peak in the structure factor, Q_{FSDP} (the analogous of the so-called first sharp diffraction peak in silica); (ii) the $Q = 30nm^{-1}$ vector corresponding to the most intense peak in the structure factor, Q_{SQMAX} . In agreement with the general MCT predictions, all correlators show a two step decay process. For times smaller than $4ps$ we observe an oscillatory decay process, from one to the non-ergodicity parameter. This time window contains all information about the microscopic dynamics and about the collective sound propagation in the Q range compatible with the simulation box size, a topic which have been studied in detail in several previous papers, independently from the MCT modelization and which will not be discussed in this article. We refer the interest reader to Refs. [27], where the frequency range above $10cm^{-1} \sim 2\pi/4 \text{ ps}^{-1}$ has been studied in detail. The second decay process, from the non-ergodicity parameter to zero, has a strong T and Q dependence. This monotonic decay (the α -relaxation) becomes slower and slower on decreasing the temperature. At the lowest simulated T , the α -relaxation is clearly separated from the microscopic time window and appears in a time region which was never explored before due to the long cpu time required to perform equilibrated molecular dynamics simulations.

To quantify the Q and T dependence of the α -relaxation we fit all correlators for times

longer than 7 ps (to avoid the interference of the oscillatory sound modes) with a stretched exponential function (Eq.10). For T higher than 230 K, the α relaxation time is smaller than 20 ps and the α relaxation process, being superimposed to the collective sound modes, can be fitted with different parameters. Instead, $F(Q, t)$ of the four lowest studied temperatures can be fitted unambiguously. The Q and T dependence of A_K , τ_K and β_K , at the lowest four studied temperatures, are shown in Fig.3, together with $S(Q)$. We note the presence of oscillations in all fitting parameters highly correlated with the oscillations in $S(Q)$.

To stress the similarity of our center of mass results with the prediction of MCT for spherical molecules we show in Fig.4 A_K, τ_K and β_K evaluated from the numerical solution of the ideal MCT coupled integro-differential equations for the Percus-Yevick solution of the hard-sphere potential. The MCT equations for the α -relaxation region [2] have been solved using the same technique as in Ref. [20]. We note that both in the theoretical hard-sphere result and in the case of SPC/E center of mass dynamics, τ_K and β oscillate in phase with the structure factor. MCT also predicts that the limit of β_K at large Q coincides with the value of the exponent b in Eq.6. From Fig.3 we note that at large Q , β_K tends to the value 0.5, the same value estimated previously on the basis of the analysis of the tagged particle motion for SPC/E water.

According to MCT, close to T_c , the T dependence of $\tau_K(Q)$ at any fixed Q should follow Eq.7. For the case $b = 0.5$, MCT predicts for γ a value of 2.7. To compare with our data, we show in Fig. 5 $\tau_K(Q)/\tau_K(Q_{FSDP})$, i.e. imposing the equivalence of the scaled time at $Q = Q_{FSDP}$. In a large Q range, i.e. $Q < 40nm^{-1}$ all curves are nicely superimposed. We note that the longest relaxation time coincides with the position of the first sharp diffraction peak, as opposed to Q_{SQMAX} . Thus, the medium range order characteristic of network forming liquids [28], is the most stable structure in the system. The enhanced stability at $Q = Q_{FSDP}$ can be predicted independently from MCT by calculating $S(Q)/Q^2$, i.e. on the basis of the so-called de Gennes narrowing. The inset in Fig.5 shows that the T dependance of the scaling factor $\tau_K(Q_{FSDP})$ is compatible with a power-law with exponent $\gamma = 2.7$ and $T_c = 202K$. We stress that the same value for γ was found for the T dependence of the self

diffusion constant, but with $T_c = 199K$. The 2% difference in T_c is within the numerical error. The time-temperature prediction of MCT, i.e. the fact that all correlators have the same T -dependence of their relaxation time is consistent with the equal value of γ found for the self and the collective dynamics in SPC/E water. As we discussed before in Ref. [11], the value of γ calculated for SPC/E is different from the one obtained by fitting the experimental data for viscosity, diffusivity or reorientational NMR times — which run from 1.6 to 2.4 on increasing the pressure. An extension of the present study at different isobars would be very valuable for clarifying the ability of the SPC/E potential to describe the dynamics of real water.

We now turn to the SPC/E dynamics in the region where the value of the correlators is not very different from the non ergodicity factor, and where according to MCT the evolution of the correlators is controlled by Eq.9. According to MCT, curves at different T but at the same Q values fall on the same master curve. Following the procedure suggested in Ref. [13] we show in Fig. 6 $F(Q, t)$ vs. $t/\tau_\alpha(T)$ where τ_α is defined by $F(Q, \tau_\alpha) = 1/e$, i.e. it is the time at which the correlation function has decayed to the $1/e$ value. From Fig. 6 it is clearly seen that, at all Q , curves for all T tends to sit on the same master curve, even the high T systems for which the α -region is hard to detect. To make the comparison with *MCT* more stringent, we compare the master curve designed by the envelope of the different samples with the universal master curve for the β -region, i.e. the solution of Eq. 2. As discussed above, the time dependence of $g(t)$ is controlled only by the value of b , via Eq.5. Thus we find that the same b value of 0.5, which was estimated from the study of self-dynamics in SPC/E water is able to rationalize both the limit value at large Q of β_K as well as the time behavior of all correlation function in the β -region. Unfortunately, no information can be obtained from our data concerning the exponent a , due to the superposition of the intense oscillations related to sound modes to the critical decay.

As predicted by the theory, the range of validity of $g(t)$ is different for different Q vectors, and appears to be larger for Q close to Q_{FSDP} and smaller for $Q_{SQMIN} = 37nm^{-1}$. The Q dependence of the correction to the master curves for large times (see Eq. 6) are also

predicted by MCT [21] and can be compared with the center of mass collective dynamics in SPC/E water. To this aim we fit $F(Q, t)$ at different Q at the lowest simulated temperature with the expression in Eq. 6 imposing $b = 0.5$, for all Q values. All correlator are fitted with the same b value. The quality of the fit is shown in Fig.7, confirming that at all Q a rather good representation of the decay of correlation in the early α -region can be obtained in terms of Eq.6. Fig. 7 shows also that the contribution of the next-to-leading order correction is not at all negligible at some Q vectors [20,21]. The result of the fit in the entire Q range are shown in in Fig.8. Fig.9 shows the same quantities calculated theoretically for the hard-sphere case (PY approximation). As in the previous qualitative comparison, both $h_{(1)}(Q)$ and $h_{(2)}(Q)$ have oscillations in phase with $S(Q)$. Results in Fig.8 clearly highlight the need of performing an analysis in term of leading and next to leading expansion to detect the correct exponent b . In any case, as already discussed in Ref. [21], $F(Q, t)$ for large Q values (large meaning larger than Q_{SQMAX}) is not a good candidate for the identification of a von-Schweidler law.

V. CONCLUSIONS

In this article we have presented evidence in favor of a MCT description of the slow collective dynamics in deeply supercooled simulated SPC/E water. The presented data concerning the collective longitudinal dynamics, together with the data in Ref. [11] concerning the self motion, offer a complete picture of the dynamics of SPC/E water under deep supercooling conditions. The evolution of the system has been studied for more than 250 ns at low T , allowing for the first time a clear identification of the two-step processes present in the correlators decay. The second decay process, clearly identified with the α -relaxation decay, is characterized by a highly non exponential behavior and by an apparent divergence of the characteristic time at a temperature around 200 K, i.e. about 50 K below the temperature of maximum density for SPC/E. An apparent divergence of the transport coefficient in real water, again at about 50 K below the temperature of maximum density, is also observed

experimentally [29,30].

The agreement between the data and MCT is striking both at qualitative and at quantitative level. At a qualitative level we have found that for both self and collective properties.

- (i) All correlators decay with a two step process which spreads over several time decades.
- (ii) The α -relaxation decay has an initial power-law behavior on leaving the plateau, whose range of validity is Q -dependent; the exponent in Eq. 9 is $b = 0.5$; unfortunately an estimate of the exponent a is not feasible, due to the overlap in time with the sound modes.
- (iii) The long times part of the decay can be well fitted by a stretched exponential function.
- (iv) The Q -dependence of the parameters in the stretched exponential (*i.e.* amplitude, time and exponent) oscillates in phase with the static structure factor, in close analogy with the MCT predictions for simple liquids.
- (v) The Q -dependence of the von Schweidler amplitude and of the next-to-leading corrections are similar to the one predicted by MCT for a hard sphere system in shape and order of magnitude.

At quantitative level we have found that

- (i) The stretching exponent β at large Q tends to 0.5, the same value as b as predicted.
- (ii) All characteristic times, both self and collective, satisfy the scaling law (Eq.7) in a large Q range; moreover, the value of the exponent γ is consistent with the value expected from the knowledge of the b exponent (Eq. 8) and it is independent from the correlator type.
- (iii) The correlator time dependence for values close to the non-ergodicity parameter is well described by the β -correlator (Eq.2).

The analysis presented here and in Ref. [11] represents an important step towards the understanding of slow structural relaxation in complex glass forming liquids, independently from the ability of SPC/E of mimicking real water. From the theoretical point of view, SPC/E is a non trivial molecular system, with molecules interacting via a strong anisotropic pair-wise additive interaction potential. Structural arrest in this system is not driven by packing constraints but by the formation of a strong network of tetrahedrally coordinated water molecules. Molecules in the cage are hindered in their translational and rotational motion by the presence of strong hydrogen bonds (energetic cages). The fact that MCT, which has been developed for simple liquids, succeeds well in describing the low T center of

mass dynamics in such a complicated molecular system, strongly supports the existence of a universality in the self and collective behavior of liquids under deep supercooling. Such universality has begun to emerge in the first applications to non-spherical molecules of the recently developed extension of the ideal MCT approach to treat angular correlators [31]; this opens the way for an even more quantitative description of the SPC/E dynamics in a MCT framework. The series of simulation here analyzed can become a clean reference system to check the novel theoretical developments.

The analysis of SPC/E water presented here and in Ref. [11] is also important in respect to the thermodynamic behavior of simulated water. We refer the interested reader to the recent book by Debenedetti [30] and to Ref. [10,9,32–34]. In this context, if SPC/E could be considered a sufficiently approximated modelling of real water, the data presented in this article would suggest that (if hopping processes did not intervene) at low pressure water would undergo a kinetic glass transition about 50 degrees below the temperature of maximum density, suggesting an interpretation of the so-called Angell temperature [7,8,3] as the critical temperature of MCT [35,11]. In this regard, the apparent power-law increase of transport coefficient in liquid water on supercooling is traced to the formation of cages and to the associated slow dynamics resulting from the presence of long living energetic cages. In other words the divergence of transport coefficients does not need to rely on a thermodynamical instability, either connected to the re-entrance of the gas-liquid spinodal or to the presence of a critical point at high pressure and low temperature [32,34] If SPC/E can represent the thermodynamic behavior of water sufficiently, we would conclude that at low pressure there is a continuous path connecting the liquid state to the low density amorphous ice.

VI. ACKNOWLEDGMENTS

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REFERENCES

- [1] For recent reviews see for example C.A. Angell, Proc. 1996 Enrico Fermi Summer School in Physics, Italian Physical Society, in press.; R. Schilling in *Disorder Effects on Relaxation Processes*, Eds. R. Richert and A. Blumen (Springer, Berlin 1994)
- [2] W. Götze, in *Liquids, Freezing and the Glass Transition*, Eds.: J. P. Hansen, D. Levesque and J. Zinn-Justin, Les Houches. Session LI, 1989, (North-Holland, Amsterdam, 1991).
- [3] C.A. Angell, in *Water: A Comprehensive Treatise*, Ed. F. Franks (Plenum, New York, 1981), Ch. 1.
- [4] E. W. Lang and H. D. Lüdemann, *Angew. Chem. Int. Ed. Engl.* **21**, 315 (1982).
- [5] A. P. Sokolov, J. Hurst and D. Quitmann, *Phys. Rev. B* **51**, 12865 (1995).
- [6] G.P. Johari, *J. Chem. Phys.* **105**, 7079 (1996).
- [7] R.J. Speedy, *J. Chem. Phys.* **86**, 982 (1982).
- [8] R.J. Speedy and C.A. Angell, *J. Chem. Phys.* **65**, 851 (1976).
- [9] S. Sastry, P. G. Debenedetti, F. Sciortino and H.E. Stanley, *Phys. Rev. E* **53** 6144 (1996).
- [10] F. Sciortino, Proc. 1996 Enrico Fermi Summer School in Physics, Italian Physical Society, in press.;
- [11] F. Sciortino, P. Gallo, P. Tartaglia, S. H. Chen, *Phys. Rev. E* **54**, 6331 (1996).
- [12] W. Götze and L. Sjögren, Special Issue of Chem. Phys. on *Rate processes with kinetic parameters distributed in time and space* Editors Y.A. Berlin, J.R. Miller and A. Plonka (1996).
- [13] W. Kob and H. C. Andersen, *Phys. Rev. E* **51**, 4626 (1995) and *Phys. Rev. E* **52**, 4134 (1995).

- [14] W. Kob, *Ann. Rev. Comp. Physics*; Vol. III, page 1., D. Stauffer Ed. (1996).
- [15] L.J.Lewis and G.Wahnstrom *Phys. Rev. E* **50**, 3865 (1994).
- [16] T. Scheidsteger and R. Schilling *Glass Transition for Dipolar Hard Spheres: a Mode Coupling Approach, Philosophical Magazine* (1997), in press.
- [17] S. Kämmerer, W. Kob and R. Schilling, preprint.
- [18] W. Götze and A. Sjögren , *Transport Theory and Statistical Physics* **24**, 801 (1995).
- [19] W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
- [20] M. Fuchs, I. Hofacker and A. Latz, *Phys. Rev. A* **45** 898 (1992).
- [21] T. Franosch, M. Fuchs, W. Götze, M.R. Mayr and A.P. Singh, *Phys. Rev. E* in print.
- [22] J.L. Barrat, W. Götze and A. Latz, *J. Phys.: Condens. Matter* **1** 7163 (1989).
- [23] J.L. Barrat J.P. Hansen and G. Pastore, *Molecular Physics* **63** 747 (1988).
- [24] U. Bengtzelius, *Phys. Rev. A* **33**, 3433 (1986).
- [25] J.L. Barrat and A. Latz, *J. Phys.: Condens. Matter* **2** 4289 (1990).
- [26] M. Nauroth, W. Kob, *Phys. Rev. E* **55**, 675 (1997).
- [27] F. Sciortino and S. Sastry, *J. Chem. Phys.* **100**, 3881 (1994) and references therein. See also F. Sette, G. Ruocco, M. Krisch, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli and R. Verbeni, *Phys. Rev. Lett.* **75** 152 (1995).
- [28] A.Uhlherr, S.R.Elliott *Philosophical Magazine B* **71**, 611 (1995).
- [29] C.A. Angell, *Ann. Rev. Phys. Chem.* **34**, 593 (1983).
- [30] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton 1997).
- [31] R. Schilling and T. Scheidsteger, preprint (1997)

- [32] P.H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, *Nature* **360**, 324 (1992).
- [33] P. H. Poole, F. Sciortino, T. Grande and H. E. Stanley, C. A. Angell, *Phys. Rev. Lett.* **73**, 1632 (1994).
- [34] F. Sciortino, P.H. Poole, U. Essmann, H. E. Stanley, *Phys. Rev. E* **55** 727 (1997)
- [35] P. Gallo, F. Sciortino, P. Tartaglia, S. H. Chen, *Phys. Rev. Letts.* **76** 2730 (1996).

FIGURES

FIG. 1. $F(Q_{FSDP}, t)$ (A) and $F_{SQMAX}, t)$ (B) vs time. $\circ T = 207. K$, $\square T = 210. K$, $\diamond T = 213.2 K$, $\triangle T = 225.0 K$, $\triangleleft T = 238.2K$, $\nabla T = 258.K$, $\triangleright T = 285.K$ Solid lines are fits with the KKW law (Eq.10) for times longer than 7 ps. Spherical average over all \vec{Q} with the same modulus has been performed for all $F(Q, t)$.

FIG. 2. $F(Q, t)$ at $T = 207K$. Q vectors are measured in units of $Q_o = 0.111nm^{-1}$. Solid lines are calculated according to Eq.10

FIG. 3. Fitting parameters of $F(Q, t)$ at $T = 207, T = 210, T = 215$ and $T = 225K$ according to the stretched exponential function Eq.10. Symbols as in Fig. 1.

FIG. 4. Fitting parameters of $F(Q, t)$ for hard-spheres (PY) from the numerical solution of the MCT equations, according to the stretched exponential function Eq.10.

FIG. 5. $\tau_K(Q)/\tau_K(Q_{FSDP})$ as a function of Q . Note that in a large Q range, all curves can be scaled on one unique curve. The continuous line is the Q dependence of collective decay times based on the de Gennes narrowing hypothesis. Symbols in the inset show the scaling factor ($\tau_K(Q_{FSDP})$) as a function of T . The full curve is the power law $\sim |T - T_c|^{2.7}$, to highlight that the T dependence of the scaling coefficient is compatible with MCT predictions, with the predicted γ value. $T_c = 202K$

FIG. 6. Master curve for $F(Q_{FSDP}, t)$ (A), $F(Q_{SQMAX}, t)$ (B), $F(Q_{SQMIN}, t)$ (C). Symbols as in Fig.1. Full line is the *beta*-correlator (the solution of the MCT equation 2 in the β -region ($g(t)$)). The dashed line indicates the $F(Q, t)$ value chosen for scaling the different T . The three selected Q have been chosen to highlight the point concerning the Q dependence of the validity of the leading expansion t^b . The validity of the β -correlator $g(t)$ is a priori limited to the region where $F(Q, t) - F_{EA}$ is small. For clarity reason we have plotted $g(t)$ in a larger range.

FIG. 7. Fit according to Eq. 6 of the $T = 207K$ correlators limited to the early α -relaxation region ($7ps < t < 800ps$), with $b = 0.5$. The fitting parameters are shown in Fig.8

FIG. 8. Q dependence of the fitting parameters $h_{(1)}$, $h_{(2)}$ to $F(Q, t)$ at $T = 207K$. (See Eq.6). $h_{(1)}$ and $h_{(2)}$ have been multiplied by τ^b and τ^{2b} respectively to take into account the difference between \hat{t} and real time. The arbitrary Q independent value of τ has been chosen to bring $h_{(1)}$ and $h_{(2)}$ in the same scale as the data of Fig.9, to make the qualitative comparison between the two set of data easier.

FIG. 9. Q dependence of F_{EA} , $h_{(1)}$ and $h_{(2)}$ for Hard-Spheres (PY) at the critical packing fraction $\eta = 0.51582$. The PY solution for $S(Q)$ is shown for reference. R is the hard-sphere radius.

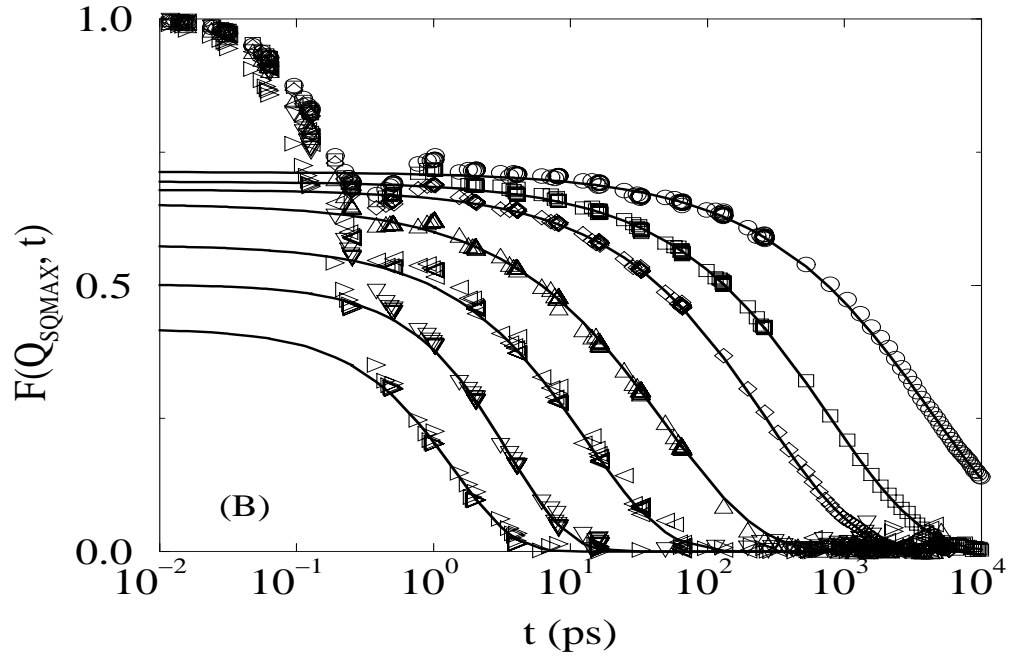
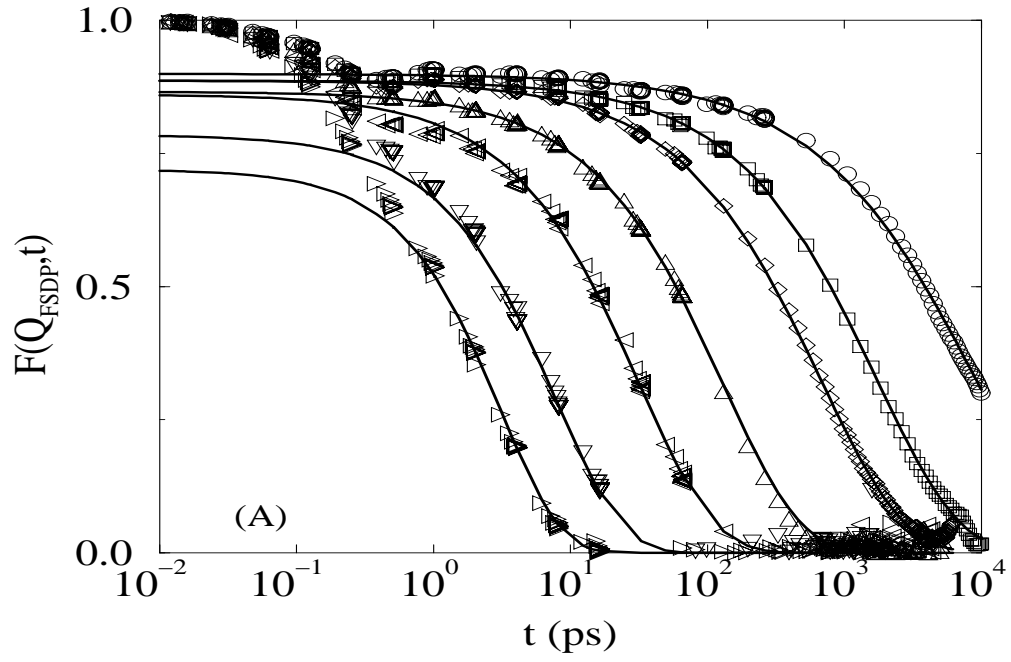


FIG. 1. F. Sciortino et al

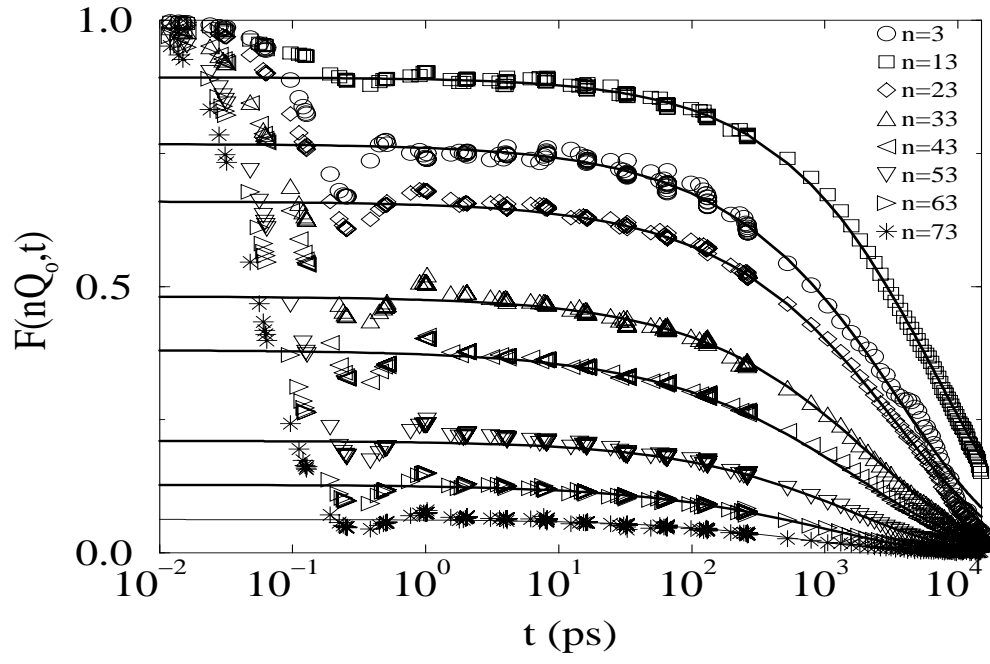


FIG. 2. F. Sciortino et al

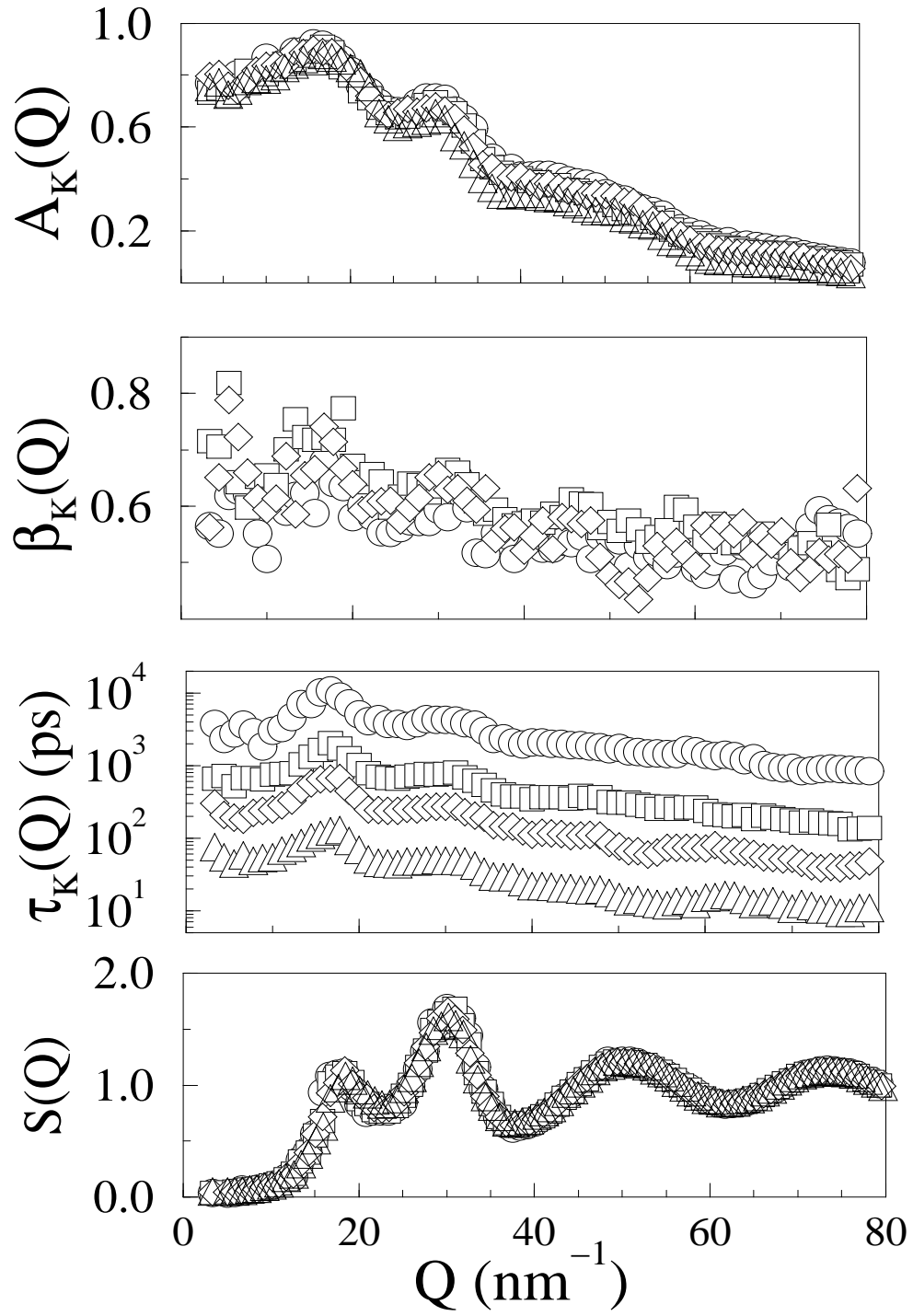


FIG. 3. F. Sciortino et al

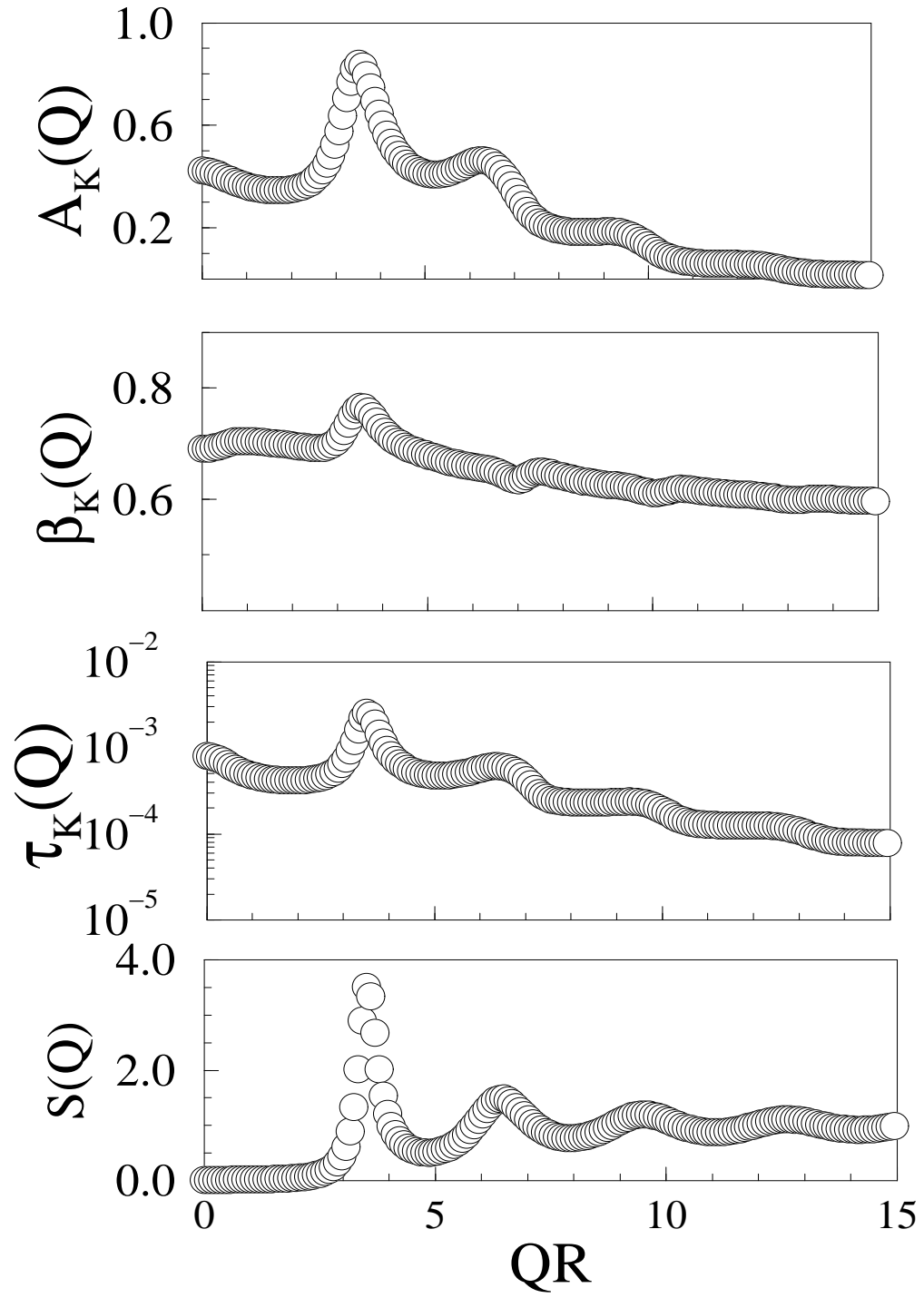


FIG. 4. F. Sciortino et al

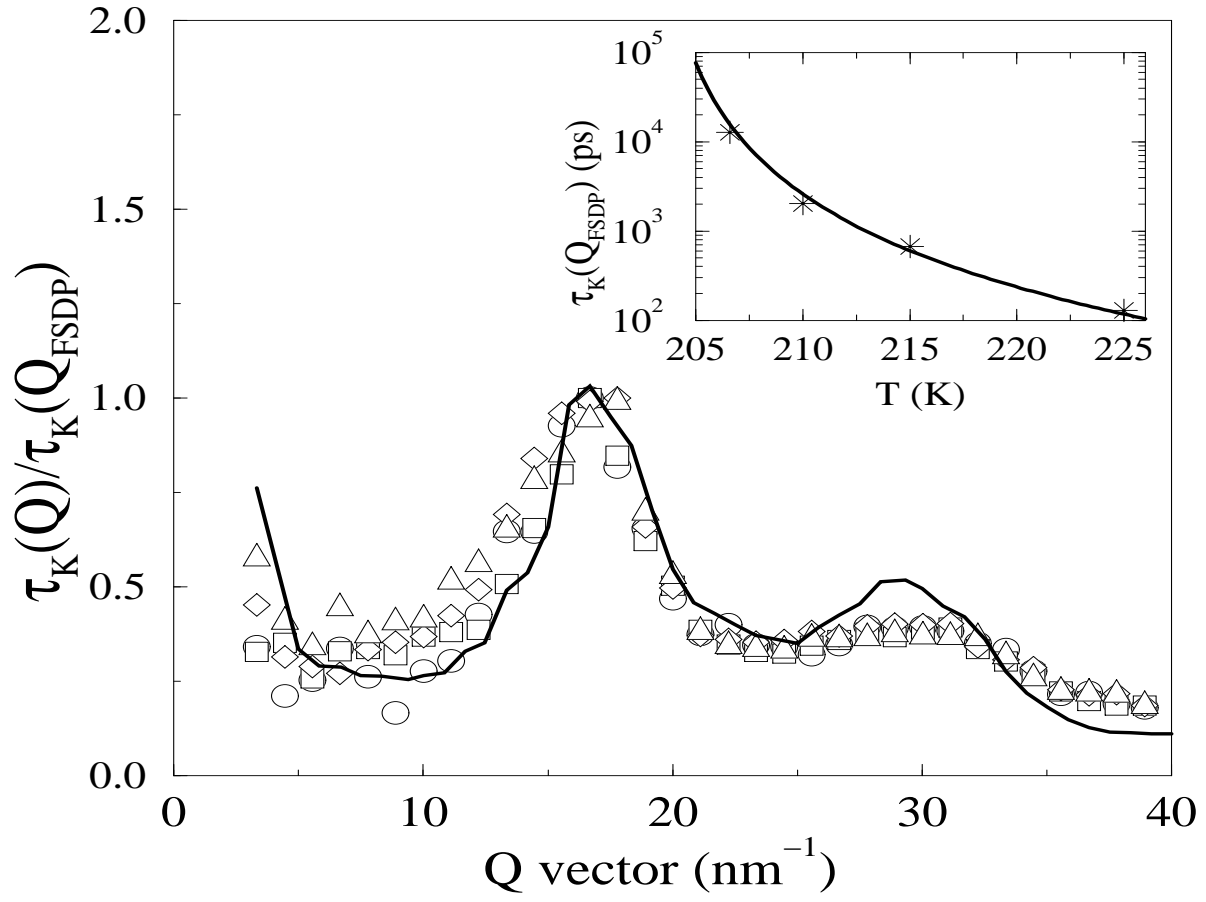


FIG. 5. F. Sciortino et al

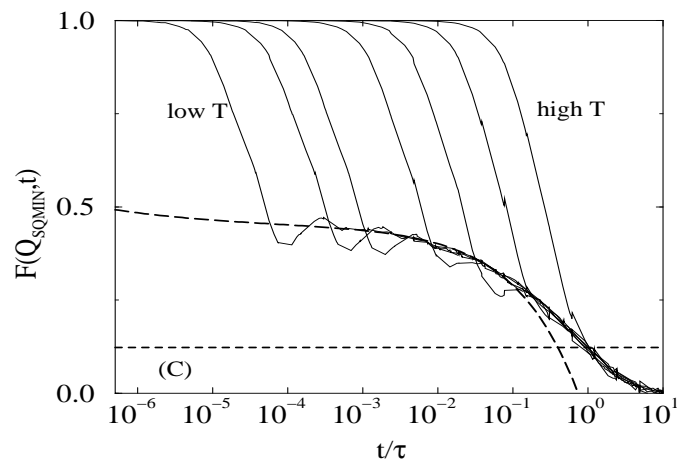
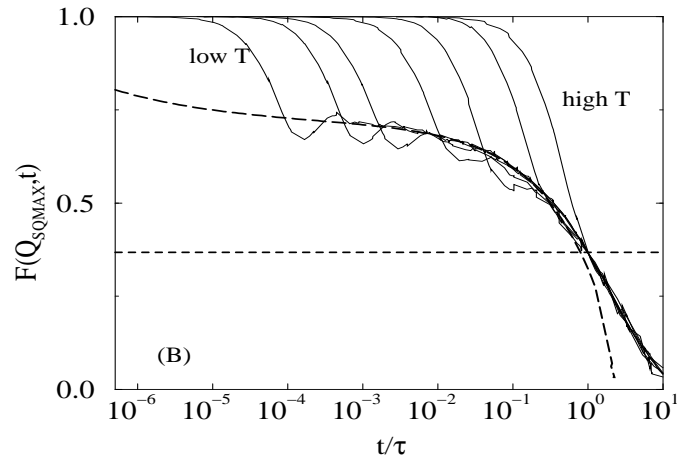
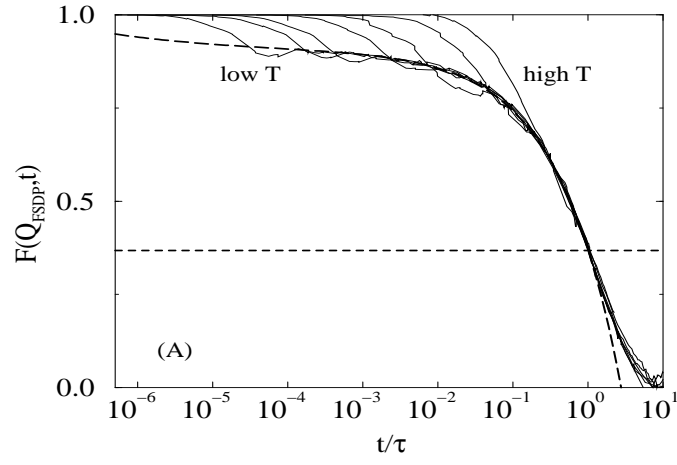


FIG. 6. F. Sciortino et al

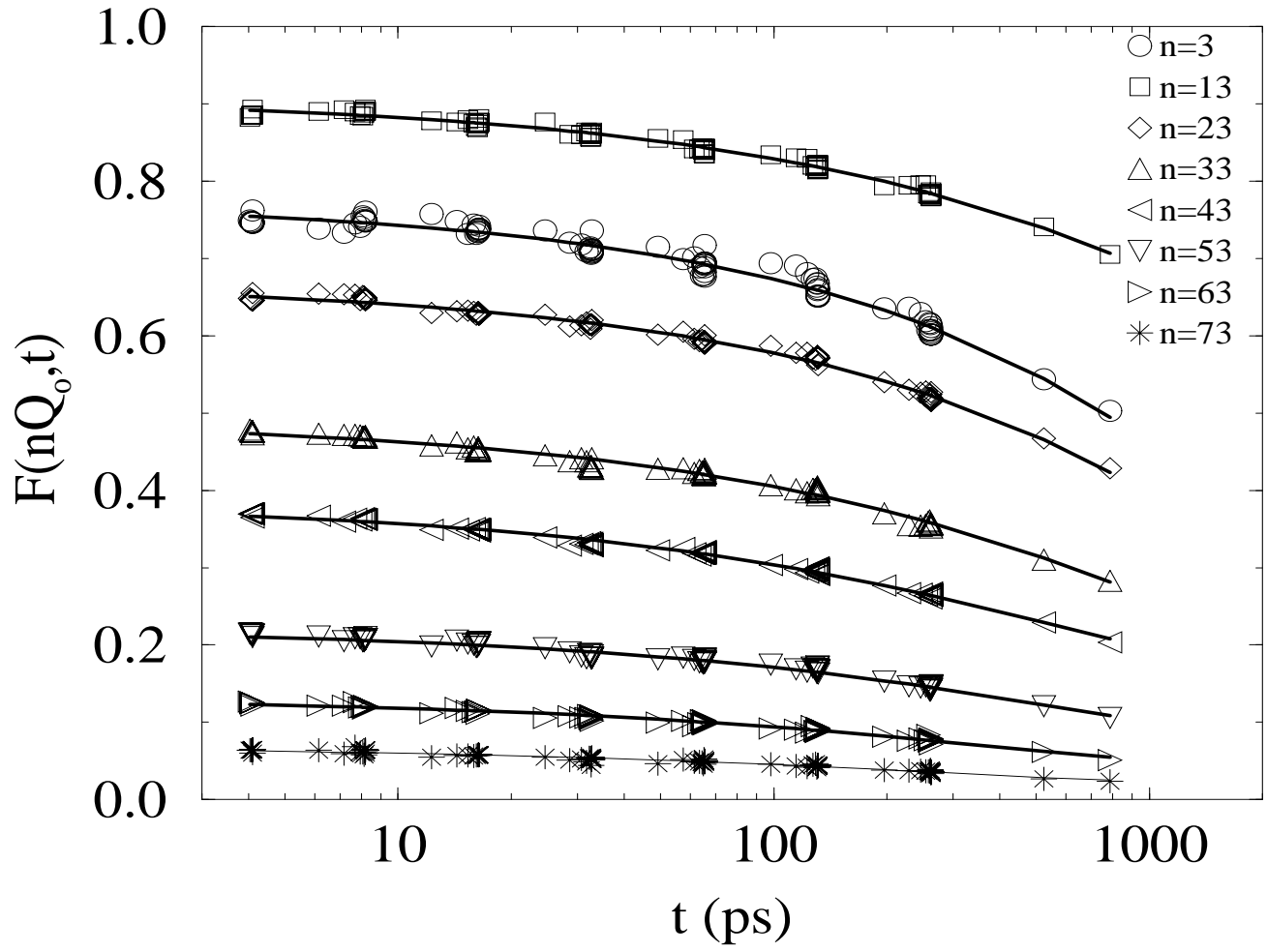


FIG. 7. F. Sciortino et al

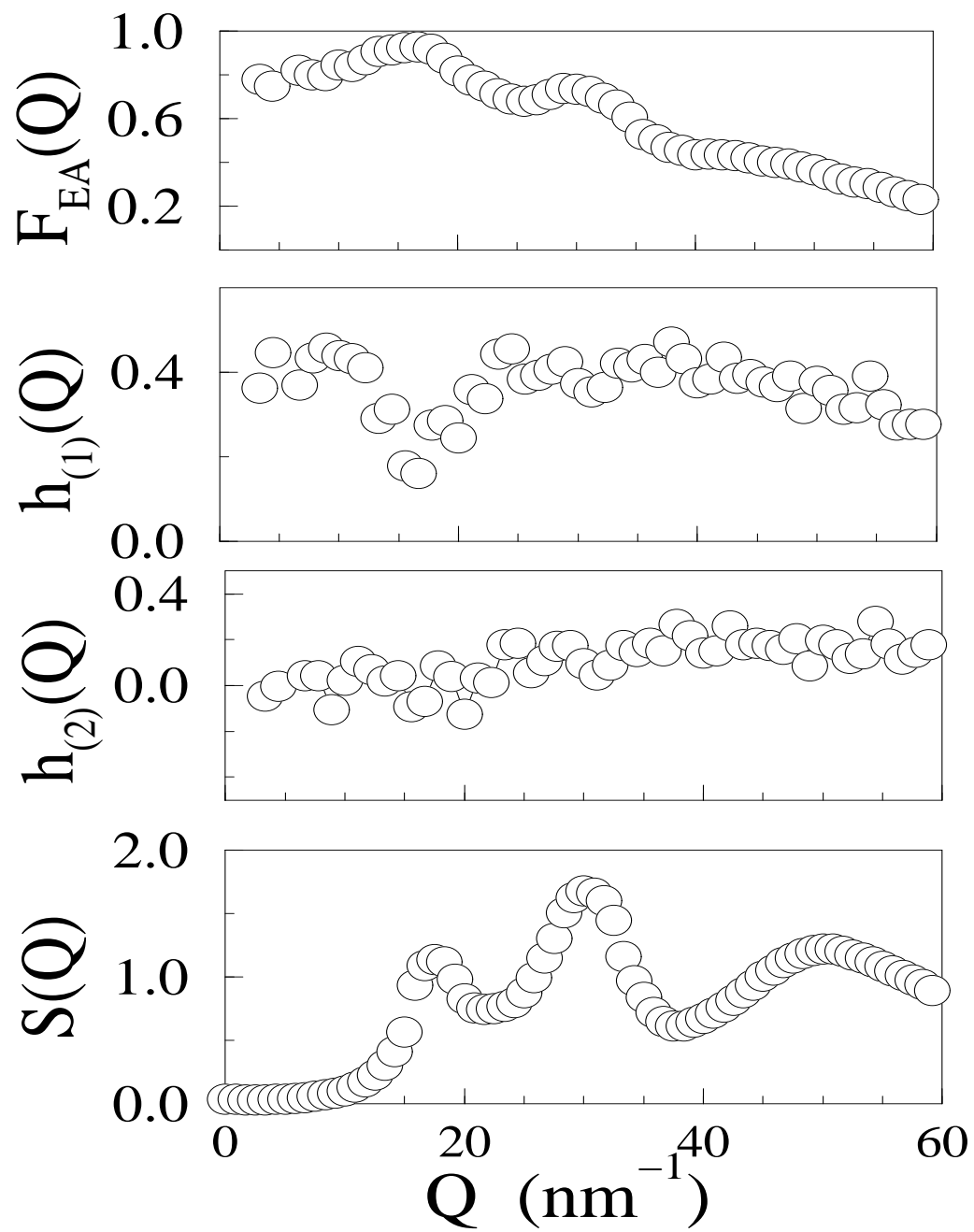


FIG. 8. F. Sciortino et al

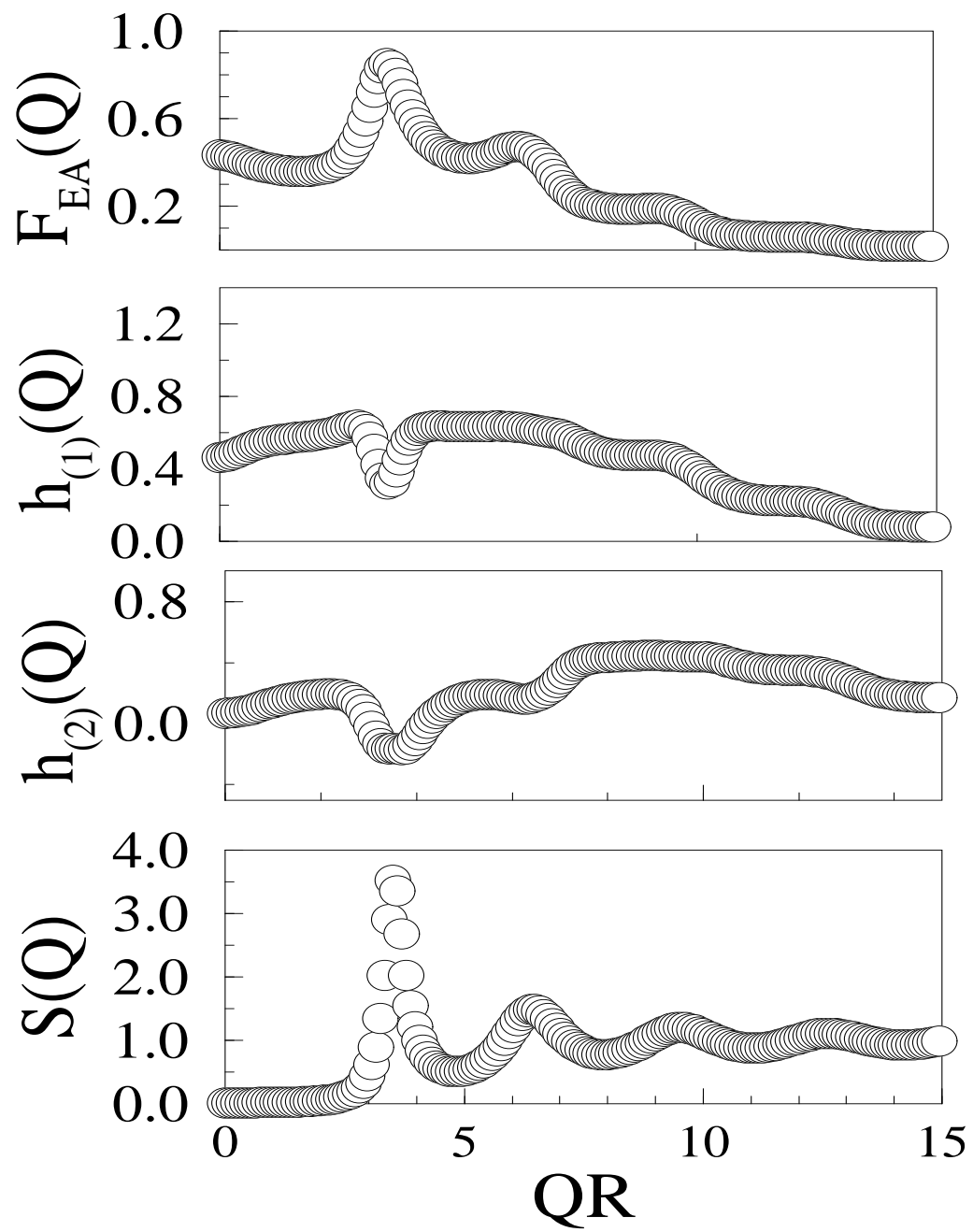


FIG. 9. F. Sciortino et al